IOSR Journal of Agriculture and Veterinary Science (IOSR-JAVS)
e-ISSN: 2319-2380, p-ISSN: 2319-2372. Volume 8, Issue 4 Ver. III (Apr. 2015), PP 66-71
www.iosrjournals.org

Evaluation of Theoretical Basis Used To Create Residual Sodium Carbonate (RSC) Equation and the Possibility of Mg-Carbonate Minerals Precipitation in Soil

Shafiek C. S. Al-Kaysi Abdulbaqi D. S. Al-Mamooree
Dept. of Soil Sci. and Water Resources,
College of Agric., Univ. of Baghdad

Abstract: *Residual Sodium Carbonate (RSC) equation which proposed by Eaton still used worldwide to evaluate the quality of irrigation waters. Eaton was suggested that both* Mg^{2+} *and* Ca^{2+} *behave in similar manner to precipitate carbonate ions in equilibrium soil – water system. The validity of this suggestion was investigated through x-ray diffraction analysis, scanning electron microscope equipped with energy dispersive x-ray analyzer (SEM-EDXRA) and chemical analysis. Examinations were conducted on disturbed and undisturbed soil samples. Both x-ray and SEM-EDXRA analyses were eliminated the possibility of magnesium carbonate precipitation in this soil, and it do not show any x-ray diffraction peak (x-ray analysis) or x-ray intensity peak (EDXRA analysis) respectively in disturbed and both disturbed and undisturbed soil samples. Fast and slow precipitation of carbonate minerals were conducted through the application of similar molar concentration of Ca or Mg or Ca + Mg applied at different concentrations and different ratio of Ca/Mg added to decalcified soil samples. Measured weight of precipitated carbonate minerals were decrease with increase in Mg ratios of added reagents. X-ray diffraction peaks of precipitated carbonates clearly indicate that calcite was the main precipitated carbonate minerals at high Ca/Mg ratio, precipitation of Mg-Calcite enhance with increase in Mg ratio of added reagents, while Mg-Calcite was the only mineral precipitated at Ca/Mg ratio 0/100. It can be deduce that most carbonate minerals precipitated in equilibrium soil-water systems were a mixture of calcite and Mg-bearing calcite minerals, contribution of magnesium in this precipitated minerals was limited compared with contribution of calcium ions. These results indicate that Eaton proposal do not consider these vital differences between* Ca^{2+} *and* Mg^{2+} *ions, and therefore RSC equation should be used cautiously.*

I. Introduction

In recent years, research efforts have been made to define the relative role of Mg^{2+}, Na^{1+} and Ca^{2+} ions in influencing soil properties and therefore in developing appropriate modifications in the criteria for quality of irrigation waters (ASCE, 2012). The addition of salts to the soil may be result in saturating the soil exchange complex with Na. The process of progressively increasing the Na-saturation of the soil exchange complex is called *sodication* (Tan, 1998). Early work by Eaton (1950) assumed that all calcium and magnesium ions would precipitate as carbonates and proposed the concept of Residual Sodium Carbonate (RSC) Which still used worldwide to evaluate the quality of irrigation waters (ASCE, 2012).

$$\text{RSC} = (CO_3^{2-} + HCO_3^{-1}) - (Ca^{2+} + Mg^{2+})$$

Where the concentration of previous mentioned ions is expressed in millimoles of charge per liter. Eaton concluded that water with RSC values over 2.5 is generally not suitable for irrigation uses, from 1.25 to 2.5 was considered marginal and with less than 1.25 safe. Sparks (2003) indicated that treated Ca^{2+} and Mg^{2+} as they were the same species is not on theoretical basis. Shainberg and Levy (2005) stated that although the RSC is still commonly reported in irrigation water analysis, its use dos not justified. They indicated that better estimate of the precipitation tendency of carbonate is provided by the so-called saturation index. One of objection on RSC equation could be the high affinity of $Ca^{2+}$to precipitate bicarbonate ions compared with Mg^{2+} (Shainberg and Levy, 2005).Christopher et al., (2009) investigate the possibility of Mg-carbonate (magnesite and dolomite) precipitation under natural conditions and concluded that this process need enough energy to remove hydration shell around Mg atoms before its precipitation in soil.

The study of the Mg-carbonate precipitation in natural conditions has been an active area of research, frequently marked by controversy over applicability to natural systems (Morse and Mackenie, 1990, Bulakh and Wenk. 2004; Nafawa and Al-Kaysi, 2006 and Thompson and Ferris, 2013). Many investigations indicates that in most soils magnesium is present in primary minerals and disqualify its precipitation as carbonate minerals as magnesite ($MgCO_3$) or nesquehonite ($MgCO_3.3H_2O$) in soil (Krauskopf, 1967; Al-Kaysi.1983; Bulakh and Wenk, 2004 and Nafawa and Al-Kaysi, 2006) while there is very limited investigations indicate the precipitation of secondary dolomite minerals in soil (Krauskopf, 1967, Nafawa and Al-Kaysi, 2006 and Kearsey, et al., 2012).

The objective of this investigation was to evaluate the validity of Eaton equation (RSC) who donates equal opportunity for magnesium and calcium ions in equilibrium soil solutions to precipitate bicarbonate ions.

II. Material and methods

Disturbed and undisturbed soil samples classified as mollic calciorthid were obtained from surface horizon located in Sayid Sadiq- Sulaimaniya Governorate. Undisturbed samples were collected using Kubiena box, and sealed in nylon bags. To prepare soil thin section the water in the samples were replaced by pure acetone and impregnated with crystic resin diluted with acetone. The mixture consisted of: acetone (1000 cm^3), crystic resin No. 17449 (100cm^3) and catalyst No. Q17447 (2 cm^3). The composition of carbonate minerals were investigated using both x-rays diffraction for disturbed soil samples and SEM – EDXRA for disturbed and soil thin section.

Disturbed soil samples (< 2 mm) were decalcifies with 1*M* sodium acetate at pH 5 as recommended by Holford and Mattingly (1975). The samples treated afterword with 0.5 *M* $CaCl_2$ at a ratio 1:20 of soil: $CaCl_2$ solution and shacked for one hour, centrifuged and the supernatant solution decanted. This procedure was repeated twice. The decalcified samples were then treated with 0.01 *M* $CaCl_2$ adjusted to pH 8 with $Ca(OH)_2$ solution in order to bring their final pH to a value close to 7.80. Finally, treated samples washed from excess salts with distilled water (two times), 95% ethanol (two times) and isopropanol (one time). A test for chloride was done using $AgNO_3$ solution to show that the samples were free from soluble salts.

Precipitation of carbonate minerals in decalcified soil samples conducted through the application of similar milliequvalents amount of Ca and / or Mg added in two different concentrations (100 and 500 mmole l^{-1}), and ratios of Ca/Mg (100/0, 75/25, 50/50, 25/75 and 0/100).These ratios respectively represent the following treatments $P_{1,}$ P_2, P_3, P_4 and P_5. Precipitation conducted through $NaHCO_3$ application which added in similar amount (as meq of HCO_3) but in two different concentrations, namely; 133.3 and 666.7 mmole L^{-1}. Fast precipitation fulfill through the use of high concentrated reagents as well as it is application directly through pipet (treatment A). Slow precipitation established through the use of diluted reagent and application of $NaHCO_3$ in slow rate as drops through burette (treatment B) as recommended by Von Wiemarn (Christian, 1980). After precipitation reactions were conducted all treatments incubated for 24h. Precipitated carbonate minerals were investigated by x-ray and it is minerals composition was differentiated quantitatively by Petersen et al., (1966) method. Concentration of calcium and magnesium were determined by atomic absorption spectrophotometry.

III. Result

The quantitative differentiation of carbonate minerals determined according to Petersen et al., (1966) method indicated that 87.8% of carbonate minerals were as calcite and the rest (12.2%) was as dolomite and Mg – bearing calcite. This data in agreement with most investigations which indicate that calcite mineral is the most abundant carbonate minerals in arid and semiarid soils (Al-Kaysi.1983 and Sposito, 2008). X-ray examination of these samples (Fig. 1) indicated the presence of calcite and possibly magnesium – bearing calcite in all investigated samples. Dolomite, however, was detected only in the < 5µm fraction of this soil. The detection of the dolomite in this fraction compared with whole soil could be facilitated by the high dolomite/calcite ratio in <5µm soil fraction (79.2% calcite and 20.8% dolomite). The low percentage of dolomite compared to that of calcite possibly affects dolomite detection. Arnaud and Herbillon (1973) have shown that the intensity of the dolomite x-ray peaks increased after calcite was preferentially removed, using H_2CO_3 – $KHCO_3$ solution. The difficulty in detecting dolomite may thus have been a result of either the absence of crystalline dolomite, or the concentration of the crystalline phase being too low to be detected by x-ray diffraction. It is also possible to interpret the data according to the model of Arnaud and Herbillon (1973). They suggested that the mole ratio of $MgCO_3$ in calcite will increase with increasing dissolution – reprecipitation cycles.

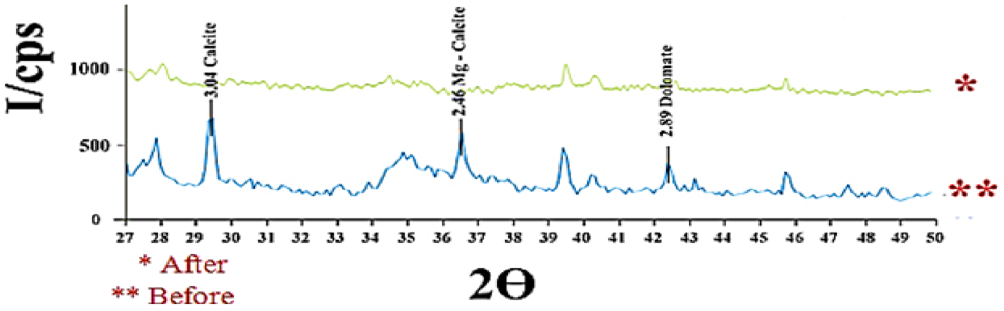

Figure 1: x-ray diffraction of Sayid Sadiq (< 5µ soil) before and after carbonate minerals removal

Minerals composition of investigated sample was conducted using soil thin section coated with graphite. Using SEM-EDXRA the intensity peak of magnesium and calcium were determined as indication of different carbonate minerals. Examined SEM-EDXRA images of disturbed soil samples (Fig. 2) and soil thin section (Fig. 3) shows that calcium carbonates exist in all investigated samples while magnesium carbonate was not detect. However, the most stable form of magnesium carbonate under highly precipitation rate in the investigated location (≅ 800 mm/year) is the crystalline nesquehonite ($MgCO_3.3H_2O$) which is more than one hundred times more soluble than calcite (Bulakh and Wenk, 2004), so it would seem reasonable to conclude that this form of carbonate would be lost from the soil to solution in this location. In addition precipitation of Mg-carbonate mineral (magnesite and nesquehonite) is doubtful under normal condition (Bohn et al., 2001 and Oelkers, et al., 2003).

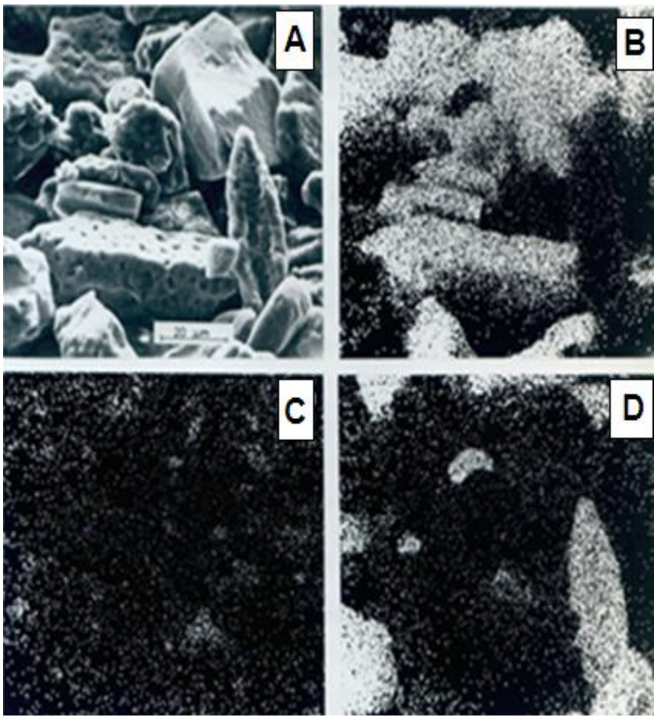

Figure 2: SEM-EDXRA image of disturbed sample (A), B, C, and D show respectively the x-ray intensity distribution of Si, Mg and Ca.

Precipitation of carbonate minerals could effect by mode of precipitation and Ca/Mg ratio in equilibrium solutions (Table 1). Fast precipitation of carbonate minerals (treatment A) were fulfilled through the application of high concentrated reagents and addition of $NaHCO_3$ in one fast dose according to Von Wiemarn principle (Christian, 1980). Precipitation of carbonate minerals were the highest in A treatments compared with B, which ascribe to the effect of precipitation mode on the physical and chemical properties of precipitated carbonate minerals. Previous investigations indicated that fast precipitation of minerals yield high number of particles possesses high specific surface area and high contamination with foreign ions (Christian, 1980 and Al-Mamooree, 2012). These properties could enhance the efficiency of carbonate minerals precipitation in A treatments compared with B.

Generally; in both treatments (A and B), the amount of precipitated carbonate minerals was decrease with increases in Mg ratio in equilibrium solutions (Table 1). This data did not in consistence with Eaton (1950) who gave a similar role for calcium and magnesium to react with carbonate ions and its precipitation as carbonate minerals. Both chemical and x-ray examination (x-ray diffraction and SEM-EDXRA analyses) conducted in this investigation indicate that this proposal is too far from their real behaviors in this complex system. Bohn, et al., (2001) indicated that Mg^{2+} is adsorbed less strongly than Ca^{2+}. They stated that calcite preferentially precipitate in soil leaving little quantity of Mg^{2+} to substitute into its structure, while dolomite precipitation as secondary minerals take place only under marine conditions. One also notes that in case of Sodium Adsorption Ratio equation ($SAR = [Na^+]/[Ca^{2+} + Mg^{2+}]^{1/2}$) Ca^{2+} and Mg^{2+} are treated as if they were the same species. Sparks, (2003) point out, that there is not a theoretical basis for this other than observation that ion valance is more important in predicting ion exchange phenomena than ion size.

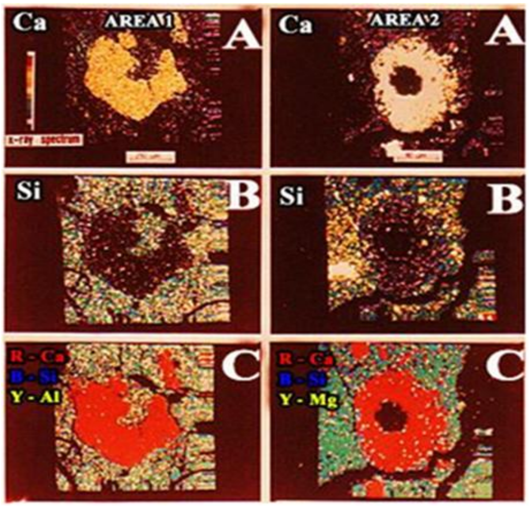

Figure 3: SEM-EDXRA images of two areas shows calcite precipitation within soil matrix (area 1x80) and around soil pore (area 2x240), (A) show x-ray image of Ca, (B) for Si, and (C) the composite images of Ca (read color), Si (blue color) and yellow color for Al (area 1) or Mg (area 2).

Calculated amounts of precipitated carbonate in all treatments were exceeded the measured values (Table 1). This data clearly indicated that not all calcium and/ or magnesium ions participate in equilibrium solution. In order to illustrate the effect of Ca/Mg ratio on the amount of precipitated carbonate minerals in different treatments, data in Figure(4) gave a value 100 for maximum weight recorded in both A and B treatments, this will display the percent change in weight of the precipitated carbonate minerals with increase in Mg ratio off added reagents. It is obvious in both fast and slow precipitation (A and B treatments) that there is enormous reduction in the amount of precipitated minerals down to 22.2% and 33.7% respectively for A and B treatments, when the ratio of add magnesium increase up to 100% in added reagents. This date confirmed by many previous studies which eliminated the precipitation of magnesium carbonate minerals in soil system under natural conditions (Bohn et al., 2001 and Oelkers, et al., 2003). Precipitation of carbonate minerals in P5 treatment ascribe to exchange of Mg with Ca on surfaces of clay minerals which precipitated as Mg-bearing calcite as indicated in x-ray examination of these samples (Fig.5).

X-ray diffractions for most treatments indicate that both calcite and Mg-bearing calcite were detected (Fig. 5). The diffractions peak at 2.10, 2.39 and 3.04A^{o} were respectively represent the first, second and third diffractions of calcite mineral. In case of P1 treatment (Ca/Mg was 100/0) figure show a sharp peak for calcite mineral. Calcite detection was clearer in A treatments compared with B especially in case of P1, P2, P3, and P4 treatments. Calcite was not detected in B treatment when Ca/Mg ratio added in the level of 25/75 (P4 treatment) this could be ascribed to the inhibition effect of Mg which prevent the precipitation of calcite in this treatment.

The effect of Mg^{2+} on calcite nucleation has been studied in many previous investigations (Berner, 1975; Morse and Mackenie, 1990 and Al-Mamooree, 2012). Under such circumstance these investigation indicate that Mg^{2+} enhance the precipitation of aragonite (Berner, 1975) and or Mg-bearing calcite. Increases in added levels of magnesium up to 100% Mg compared with zero level of Ca (treatment P5) did not show any peak for calcite in both A and B treatments, while gave obvious peaks for Mg-bearing calcite at d-spacing 2.46 A^{o}. However; the intensity of diffraction peaks for Mg-bearing calcite increase with increase in the level of Mg added to the soil, whereas the intensity of calcite peaks decline. x-ray examination for all treatments did not detect any crystal formation of dolomite or any kind of Mg-carbonate minerals.

Table (1): the effect of precipitation mode on quantity of carbonate minerals precipitated (mg g^{-1} soil) in each treatment.

$\frac{Ca}{Mg}$Ratio Mode of precipitation	P1	P2	P3	P4	P5	Mean
A*	138.2	107.1	81.3	48.9	30.7	81.2
A$^{\#}$	143.1	113.8	90.0	60.7	35.9	88.7
B*	91.7	89.9	73.1	42.7	30.9	65.7
B$^{\#}$	109.9	96.1	87.1	55.9	33.7	76.5

***calculated from the increase in oven dry weight of soil after precipitation reactions had been conducted.**

 # the amount of carbonate minerals precipitated in equilibrium system calculated from the amounts of Ca, Mg or Ca + Mg add to the soil system – its amount in equilibrium solutions x M.W of precipitated carbonate minerals / atomic weight of added ions (Ca^{2+} or Mg^{2+} or Ca^{2+} and Mg^{2+}).

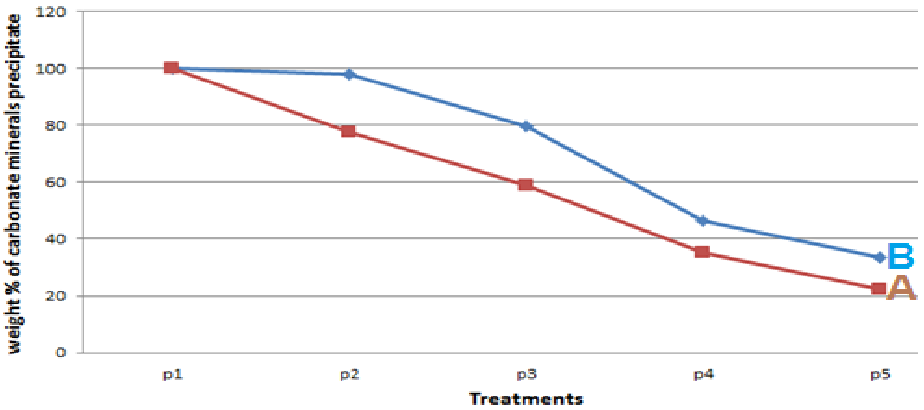

Figure 4: Effect of Ca/Mg ratio on weight %of precipitated carbonate minerals.

It's clear from previous data that Eaton proposal who gave equal opportunity for calcium and magnesium to precipitate carbonate ions in soil-water system did not put on real scientific basis. Precipitation of carbonate ions (CO_3^{2-}) mainly determined by calcium ions (Fig.4) which precipitated as $CaCO_3$ (calcite) at low Mg ratio or as calcite and Mg-bearing calcite at high Mg ratio or mainly as Mg-bearing calcite at very high Mg ratio in equilibrium solutions (Fig 5). There is no evidence that CO_3^{2-} could precipitated as Mg–carbonate by its self as a separate minerals. It's important to consider this vital point as a significant limitation in RSC equation before we consider its value in our evaluations for the quality of irrigation waters.

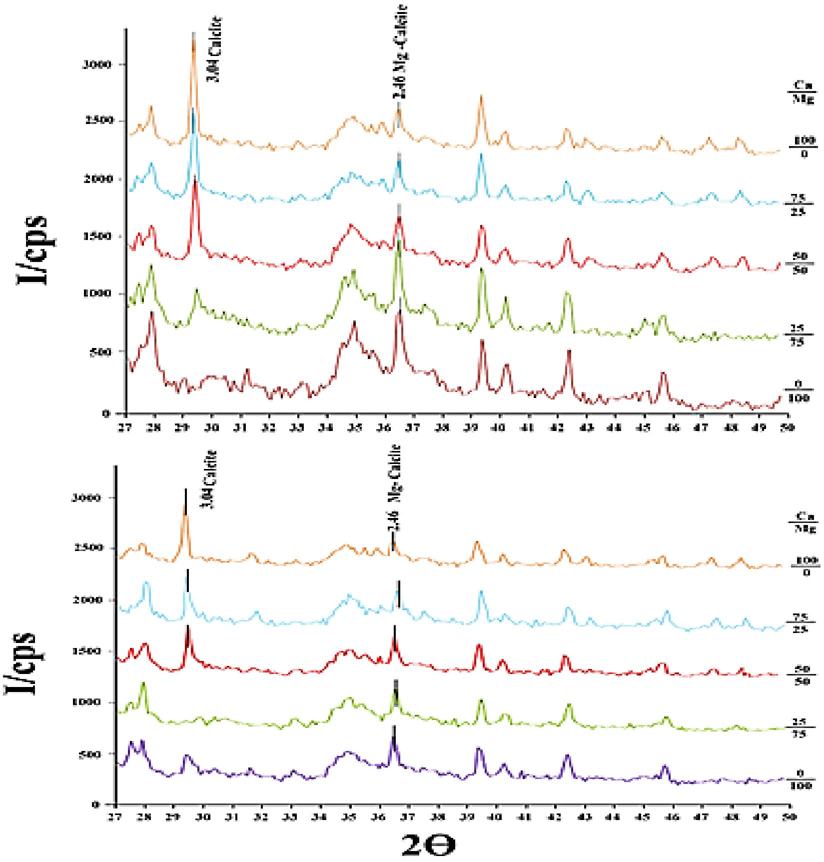

Figure 5: x-ray diffraction of precipitated carbonate minerals in different treatments.

References

[1]. Al-Kaysi, S.C. (1983). Physical and chemical characterization of carbonate minerals in Iraqi soils. Ph. D. Thesis, Dept. of Soil Sci. Newcastle Upon Tyne, U.K.

[2]. Al-Mamooree, A. D. S. 2012. Role of precipitation pattern, Ca/Mg ratio and ionic strength in properties of carbonate minerals and it is effect in zinc adsorption. . Ph. D. Thesis, Dept. of Soil Sci. and Water Resources, College of Agriculture, University of Baghdad, Iraq.

[3]. Arnaud, R.J., and A.J. Herbillon. (1973). Occurrence and genesis of secondary magnesium bearing calcites in soil. Geoderma. 9:279-298.

[4]. ASCE. 2012. Agricultural Salinity Assessment and Management. ASCE Manuals and Reports on Engineering Practice No. 71. American Society of Civil Engineers.

[5]. Berner, R.A. (1975).The role of magnesium in the growth of calcite and aragonite from sea water.Geochim.Cosmochim.Acta. 39:489-504.

[6]. Bohn, H.L.; McNeal, B. L. and O‘onnor, G. A. 2001.Soil chemistry. John Wiley and Sons, Inc.

[7]. Bulakh, A. and H-R.Wenk. 2004. Minerals: Their constitution and origin.

[8]. University Press, Cambridge. UK.

[9]. Christian, G.D. (1980). Analytical chemistry.3rd Edition. J. Wiley and Sons., Inc. N.Y.

[10]. Christopher , S. R; C. J. Lopez; A. R. Navarro; N. Sahi and M. Coleman.(2009). Inorganic synthesis of Fe-Ca-Mg carbonate at low temperature. Geochimica Cosmochimica . 73:5361-5376.

[11]. Eaton, F. M. 1950. Significant of carbonates in irrigation waters. Soil Sci. 69:123-133.

[12]. Holford, I.C.R., and G.E.G. Mattingly. (1975). Surface areas of calcium carbonate in soils. Geoderma 13:247-255.

[13]. Kearsey, T., R.J. Twitchett, and A.J. Newell. 2012. The origin and significance of pedogenic dolomite from the upper permian of the Urals Russia. Geological Magazine, 129:291-307.

[14]. Krauskopf, K.B. 1967. Introduction to geochemistry. McGraw-Hill, Inc., New York.

[15]. Morse, J. W. and F. T. Mackenie. 1990. Geochemistry of sedimentary carbonate. Elsevier Science Publishers, B.V.

[16]. Nafawa, Sh. M. and S. C. Al-Kaysi. 2006. Geochemistry of carbonate minerals equilibrate with different concentrations of salts in saturated CO_2 environment. Iraqi J. of Soil Sci., 6(1): 80-92

[17]. Petersen , G. W. G. Chesters and G. B. Lee 1966. Quantitative determination of calcite and dolomite in soil. J. Soil Sci., 17:328-338.

[18]. Oelkers, E., J. Scott and O. Pokrovsky. 2003. The dissolution and precipitation rates of magnesite as a function of solution composition at 150℃ and implications for CO_2 sequestering. EGS- AGU-EUG Joint Assembly, Abstracts from the meeting held in Nice, France, 6-11 April 2003.

[19]. Shainberg, I. and Levy, G.J. (2005).Flocculation and Dispersion.Vol. 2 p. 27-34. In Hillel, D. (ed-in-chief). Encyclopedia of Soils in the Environment Elsevier Ltd., Oxford, U.K.

[20]. Sparks, D.L. 2003. Environmental Soil Chemistry, 2rd Edition, Academic press.

[21]. Sposito, G. 2008. The chemistry of soils.2rd Edition.Oxford University Press.

[22]. Tan, K. H. 1998. Principles of soil chemistry.3rd Edition. Marcel Dekker, Inc.

[23]. Thompson, J. B. and F. G. Ferris. 2013. Cyanobacterial precipitation of gypsum, calcite, and magnesite from natural alkaline lake water. Geology, 18 (10): 995-998.